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European Patent Office
Office européen des brevets



(11) Publication number : **0 330 272 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification :
29.07.92 Bulletin 92/31

(51) Int. Cl.⁵ : **C09J 7/02**, **C08L 23/28**,
C08L 27/06

(21) Application number : **89200393.0**

(22) Date of filing : **17.02.89**

(54) **Thermoplastic, plasticizer-resistant film, and pressuresensitive film comprising the plasticizer-resistant film.**

(30) Priority : **19.02.88 NL 8800428**

(43) Date of publication of application :
30.08.89 Bulletin 89/35

(45) Publication of the grant of the patent :
29.07.92 Bulletin 92/31

(84) Designated Contracting States :
BE DE ES FR GB IT NL SE

(56) References cited :
EP-A- 0 060 667
EP-A- 0 103 407
EP-A- 0 201 890
FR-A- 2 177 910
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5th Ed. vol. 11, p. 235-236 (1985)

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EP 0 330 272 B1

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Description

This invention relates to a pressure-sensitive film adapted for adherence to a vinyl substrate plasticized with monomeric plasticizer.

5 Vinyl substrates plasticized with monomeric plasticizer have found extensive use for interior surface such as wall coverings and exterior surfaces such as vinyl coated canvas for trucks. These vinyl substrates contain as much as 25-75 parts of monomeric plasticizer per 100 parts of vinyl resin. Letters, figures or drawings are applied to said vinyl substrates by hand painting or by printing with screen printing inks. For this purpose also a pressure-sensitive vinyl film optionally printed with letters, etc., can be used. In the latter case the vinyl film tends to wrinkle and to turn sticky, and the adhesive layer tends to loose adhesion. These problems are substantially attributable to the migration of plasticizers from the substrate into the film.

EP-A-0103407 discloses a pressure-sensitive film adapted for adherence to vinyl substrates plasticized with monomeric plasticizer. This film comprises a first layer of polyvinyl chloride, a second layer of a plasticizer-resistant, pressure-sensitive adhesive and a third layer between said first and second layers serving as a barrier for migration of the plasticizer from the vinyl substrate. This film meets the following demands: it is capable of maintaining adhesion and a wrinkle free surface, when adhered to a plasticizer substrate, and is receptive to screen printing inks as commonly used for printing PVC films.

EP-A-0201890 discloses a composite film comprising, as a first layer, a blend of a vinyl chloride polymer and a chlorinated polyolefin and, as a second layer, a normally solid thermoplastic adhesive. Said film is preferably employed as a weatherable surface coating for aluminum or steel sheet substrates. The adhesive layer only has adhesive properties when heated, e.g. to 220°C.

EP-A-0060667 discloses a film comprising a layer of an internally plasticized vinyl chloride copolymer resin and a layer of pressure-sensitive adhesive. The vinyl chloride copolymer layer may contain chlorinated polyethylene as a process aid in an amount of 2-15% by weight.

25 FR-A-2,177,910 discloses a process for the preparation of a polyvinyl chloride film suitable for the manufacture of adhesive tape. The polyvinyl chloride layer comprises chlorinated polyethylene in an amount of 1-10% by weight to improve the impact resistance.

The present invention provides a pressure-sensitive adhesive film combination consisting of only two layers which film meets the three-layer product performance of EP-A-0103407. The present pressure-sensitive film comprises a first layer consisting of a blend of polyvinyl chloride and chlorinated polyethylene and a second layer consisting of a plasticizer-resistant, pressure-sensitive adhesive.

Accordingly, the present invention provides a composite film comprising two layers, the first layer comprising a blend of polyvinyl chloride and chlorinated polyethylene in respective weight ratios of 10:90 to 90:10 in which the polyvinyl chloride has a K-value of from 45 to 80 and the chlorinated polyethylene has a chlorine content of from 30 to 45% by weight and the second layer consisting of an adhesive, characterized in that the second layer consists of a plasticizer-resistant, pressure-sensitive adhesive comprising the polymeric reaction product of monomers comprising (a) acrylic acid, methacrylic acid, acrylamide and/or methacrylamide, (b) an alkylacrylate and/or alkylmethacrylate and (c) at least one additional unsaturated monomer.

The pressure-sensitive film according to the invention meets the three previously mentioned product demands. First, the blend of polyvinyl chloride and chlorinated polyethylene is receptive to screen printing inks as commonly used for printing polyvinyl chloride films. Owing to the lack of a barrier layer monomeric plasticizer will diffuse from the vinyl substrate into the film. However, the plasticizer concentration will reach an equilibrium. Surprisingly this concentration of plasticizer does not lead to a sticky or wrinkling film or adversely impact the pressure-sensitive adhesive layer.

45 Hereinafter a more detailed description of both the thermoplastic, plasticizer-resistant film and the pressure-sensitive adhesive layer according to the invention will follow:

A suitable weight ratio of polyvinyl chloride:chlorinated polyethylene is 10:90 to 90:10, preferably 35:65 to 65:35. The ratio of polyvinyl chloride:chlorinated polyethylene which gives the best film properties, depends on other parameters, such as the K-value of the polyvinyl chloride, the melting viscosity of the chlorinated polyethylene and the processing conditions of the polymer blend. Thus, using polyvinyl chloride having a high K-value relatively more chlorinated polyethylene is necessary to get good film properties.

The already mentioned K-value or inherent viscosity of the polyvinyl chloride is a measure of the average molecular weight (See "Encyclopedia of Polymer Science and Technology", Vol. 14, John Wiley & Sons (1971)). This K-value can amount to 45-80, preferably to 50-65. By applying polyvinyl chloride having K-values higher than 80 it costs much power to prepare a blend having the required distribution of polyvinyl chloride and chlorinated polyethylene. In addition in that case a somewhat more rigid film is produced.

The polyvinyl chloride can be prepared in any conventional manner, that is by suspension-, mass- or emulsion polymerisation. Usually polyvinyl chloride produced by suspension polymerisation is used.

The chlorinated polyethylene that is applied, can be produced according to known methods by chlorination of polyethylene. Suitable chlorinated polyethylenes have a chlorine content of 30-45% by weight and preferably about 42% by weight, and a melting viscosity of 600-3,000 Pa.s.

The blend of chlorinated polyethylene and polyvinyl chloride usually comprises furthermore UV- and/or heat-stabilizers, antioxidant, pigment or other usual additives. Plasticizers are in general not present or substantially not present because of the plasticizing effect of the chlorinated polyethylene. Ethylene/vinyl acetate copolymers in an amount of up to 10% by weight may be added to the polymer blend without affecting the properties of the film.

The blend of chlorinated polyethylene and polyvinyl chloride may be prepared with any conventional blending apparatus. Therefore the two polymers in the appropriate amount in the form of for example powders together with further usual additives are added to the blending apparatus. The blend is thoroughly mixed until a homogeneous melt is obtained, preventing decomposition of primarily the polyvinyl chloride. Subsequently a film is manufactured from the homogeneous melt by any conventional manner including casting, extruding and calendaring. The thickness of said film may be 0.01-0.15 mm and preferably 0.06-0.10 mm.

The adhesive used in the pressure-sensitive film according to the invention, must be pressure-sensitive (self-adhesive) and plasticizer-resistant; the latter means that the adhesive should have an adhesion level which is sufficiently high independent of the plasticizer concentration.

The previously mentioned European patent specification 103 407, incorporated herein by reference, discloses adhesives functional for this purpose. Generally, adhesives which have proved to function, comprise polymers of a combination of the following monomers: acrylic acid, methacrylic acid, acrylamide, methacrylamide (preferably present in amounts from 1.0% to about 10% by weight), alkyl acrylates, alkyl methacrylates containing at least 4 carbon atoms (preferably present in amounts of about 35% to 85% by weight), and other unsaturated monomers, like N-vinyl pyrrolidone (5 to 15% by weight), methyl acrylate (15 to 50% by weight) and vinyl acetate (20.0-50.0% by weight). Fumaric acid and/or mono- and diesters of unsaturated dicarboxylic acids like dibutyl fumarate may also be present.

A specific adhesive composition found suitable in the practice of this invention is a terpolymer made from 52.2 parts n-butylacrylate, 37.5 parts methyl acrylate, and 10 parts of acrylic acid. For economy this adhesive may be prepared at a low inherent viscosity and cross-linking agent. Another adhesive found suitable in the practice of this invention is a linear terpolymer consisting of 56.0 parts of isooctylacrylate, 40.1 parts of vinyl acetate and 4.0 parts of acrylic acid. Yet another adhesive is a terpolymer prepared from 85.0 parts of n-butylacrylate or methylbutylacrylate, 10.0 parts of N-vinyl pyrrolidone and 5.0 parts of acrylic acid.

The best results are obtained when such a polyacrylate is blended with a certain amount, preferably 10-35%, of a phthalic acid ester of hydro-abietyl alcohol and with a certain amount, preferably 0.5-5%, of a dialkyl phthalate.

The polyacrylate and the additional blends are present in the form of a 25-35% solution in suitable solvents, like isopropanol, hexane, toluene, ethyl acetate, etc. The required crosslinking is effected with conventional methods such as irradiation by electron beams or addition of metal organic compounds such as aluminum acetyl acetonate to the solution.

The adhesive is in general present in an amount of 20-70, preferably 30-50 g/m² film. The adhesive can be applied to the film by any conventional coating method to obtain a regular distribution of the adhesive upon the surface.

Test methods

In the following Example the pressure-sensitive films manufactured according to the invention are subjected to the following tests:

1. 90° peel adhesion

The adhesion is the force needed to peel a pressure-sensitive film applied to a substrate. Test specimen having a length of 150 mm and a width of 25 mm are used, and the adhesion is determined in N/25 mm. Test specimen are peeled under 90° at a rate of 300 mm/min. using a tester at a temperature of 23 ± 2°C. The test is carried out 24 hours after applying to the substrate, in which time the adhesion has been sufficiently built up. In addition the test is carried out after 3 weeks (accelerated) ageing of adhered film and substrate at 70°C in a hot air oven.

It is assumed that 3 weeks at 70° C is highly sufficient to produce an equilibrium situation of the plasticizer distribution in substrate, adhesive and PVC/CPE (Polyvinyl chloride/Chlorinated polyethylene) -layer, as will

be reached in practice after a period of time.

2. Appearance

5 Appearance of adhered film is evaluated after staying in a hot air oven at 70°C for 1,2 and 3 weeks; reference is an unaged film. Evaluation criteria are wrinkling, shrinkage and stickiness of the PVC/CPE layer. All the films mentioned in the Example were evaluated as good after 3 weeks at 70°C.

3. Flexibility

10 As there is no standard test for evaluation of the flexibility the flexibility is provisionally evaluated by manual movement. It appeared that films wherein the amount of chlorinated polyethylene was somewhat higher and the K-value of the polyvinyl chloride was somewhat lower, are most satisfactory.

15 Example

 A number of representative pressure-sensitive films according to the invention has been manufactured. The first layer consisting of a blend of chlorinated polyethylene and polyvinyl chloride has a thickness of 100 µm. The types of polyvinyl chloride (prepared by suspension-, mass- or emulsion- polymerisation, s, m and e respectively), the K-value of the PVC, the chloride content of the CPE and the weight ratio of PVC/CPE are mentioned in the following table. The PVC/CPE-blends comprise per 100 parts by weight a stabilisation package consisting of 1.5 part by weight of heat-stabilizer, 1 part by weight of UV-stabilizer, 0.5 part by weight of antioxidant, 1 part by weight of processing aid (methacrylate) and 2.5 parts by weight of fatty acid esters.

25 The PVC/CPE-layer is provided in a conventional way with such a layer of adhesive that the weight of the adhesive regularly distributed upon the surface is 40 g/m². The adhesive composition is 72% by weight of polyacrylate made from 2-ethylhexylacrylate, vinylacetate and acrylic acid, 24% by weight of phthalic acid ester of hydro-abietyl alcohol, 3.5% by weight of dialkyl phthalate and 0.5 % by weight of aluminum acetyl acetonate.

 The resulting pressure-sensitive films are laminated on vinyl substrates. The basis of the substrates (tarpaulins) used in the tests is a woven canvas structure, to which and within which plasticized PVC is applied. The tarpaulins may optionally be provided with coatings. Said coatings (acrylate) affect indeed the adherence level which does not have very large consequences for the initial adherence, but they do affect distinctly the adherence as a function of time, as said coatings somewhat provide diffusion barriers which means that the equilibrium situation is reached less rapidly. This is also shown by plasticizer concentration determinations at certain times of accelerated ageing in identical film samples adhered to coated and uncoated plasticized PVC-substrates. This means that pressure-sensitive films adapted for application on uncoated plasticized PVC-substrates are certainly adapted for application on coated plasticized PVC-substrates.

35 The concentration of plasticizer in the PVC of the substrate is 30-40% by weight. All the used plasticizers are phthalic acid esters of alkanols having at least 8 carbon atoms. Frequently applied plasticizers are dioctyl phthalate and didecyl phthalate, the first mentioned having the highest diffusion rate in otherwise identical conditions.

40 The substrate used for ageing comprises a blend of substantially these two plasticizers.

 The adherence level of the pressure-sensitive film with the substrate after lamination and 24 hours at room temperature to build up said adherence is satisfying for all these films and it varies between 11 and 17 N/25 mm. The constructions comprising substrate, adhesive layer and PVC/CPE-layer as indicated in the table are subjected to accelerated ageing for three weeks (500 hours) at 70°C. After said ageing the adherence of the pressure-sensitive films with the substrates is determined:

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90° Peel adhesion
(after ageing)

PVC/CPE

CPE

PVC

uncoated substrate
coated substrate

(N/25 mm) (N/25 mm)

(% by weight)

(% by weight)

K-value

type

s	50	42	40/60	21.9	10.4
s	50	36	20/80	12.5	10.0
s ¹	50	42	45/55	10.1	9.8
m	58	36	40/60	8.0	7.0
s	58	42	40/60	9.0	8.4
e	60	42	40/60	8.1	9.1
m	60	36	40/60	12.6	7.4
m	60	42	20/80	8.7	8.4
s	65	36	60/40	14.2	8.5
s	70	36	80/20	7.9	7.8
s	80	36	20/80	15.7	11.1
s	80	42	20/80	11.9	9.3

1 = addition of 25% parts by weight of titanium dioxide (rutile) per 100 parts
by weight of PVC./CPE.

Claims

- 5 1. A composite film comprising two layers, the first layer comprising a blend of polyvinyl chloride and chlorinated polyethylene in respective weight ratios of 10:90 to 90:10 in which the polyvinyl chloride has a K-value of from 45 to 80 and the chlorinated polyethylene has a chlorine content of from 30 to 45% by weight and the second layer consisting of an adhesive, **characterized in that** the second layer consists of a plasticizer-resistant, pressure-sensitive adhesive comprising the polymeric reaction product of monomers comprising (a) 10 acrylic acid, methacrylic acid, acrylamide and/or methacrylamide, (b) an alkylacrylate and/or alkylmethacrylate and (c) at least one additional unsaturated monomer.
2. A composite film according to claim 1, **characterized in that** the weight ratio of polyvinyl chloride : chlorinated polyethylene is from 35 : 65 to 65 : 35.
3. A composite film according to claims 1 or 2, characterized in that the polyvinyl chloride has a K-value 15 of from 50 to 65.
4. A composite film according to any of claims 1 to 3, **characterized in that** the chlorinated polyethylene has a chlorine content of about 42% by weight.
5. A composite film according to any of claims 1 to 4, **characterized in that** the adhesive is applied at a coat weight of 30 to 50 g/m².
- 20 6. A composite film according to any of claims 1 to 5, **characterized in that** the adhesive includes from 0.5 to 5% by weight of a dialkyl phthalate and from 10 to 35% by weight of a phthalic acid ester of hydroabietyl alcohol.

25 Patentansprüche

1. Verbundfolie mit zwei Schichten, wobei die erste Schicht eine Mischung aus Polyvinylchlorid und chloriertem Polyethylen in entsprechenden Gewichtsverhältnissen von 10:90 bis 90:10 aufweist, in welcher das Polyvinylchlorid einen K-Wert von 45 bis 80 und das chlorierte Polyethylen einen Chlor-Anteil von 30 bis 45 30 Gew.-% hat, und wobei die zweite Schicht aus einem Klebstoff besteht, **dadurch gekennzeichnet**, daß die zweite Schicht aus einem für Weichmacher unempfindlichen, druckempfindlichen Klebstoff mit dem polymeren Reaktionsprodukt von Monomeren besteht, welche (a) Acrylsäure, Methacrylsäure, Acrylamid und/oder Methacrylamid, (b) ein Alkylacrylat und/oder Alkylmethacrylat und (c) mindestens ein zusätzliches ungesättigtes Monomer aufweisen.
2. Verbundfolie nach Anspruch 1, **dadurch gekennzeichnet**, daß das Gewichtsverhältnis von Polyvinylchlorid zu chloriertem Polyethylen im Bereich von 35:65 bis 65:35 liegt.
3. Verbundfolie nach den Ansprüchen 1 oder 2, **dadurch gekennzeichnet**, daß das Polyvinylchlorid einen K-Wert von 50 bis 65 hat.
4. Verbundfolie nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß das chlorierte Polyethylen einen Chlor-Anteil von etwa 42 Gew.-% besitzt.
5. Verbundfolie nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß der Klebstoff bei einem Flächengewicht von 30 bis 50 g/m² aufgebracht ist.
6. Verbundfolie nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß der Klebstoff 0,5 bis 5 Gew.-% an Dialkylphthalat und 10 bis 35 Gew.-% an Phthalatsäureester von Hydroabietylalkohol enthält.

Revendications

1. Film composite comportant deux couches, la première couche comprenant un mélange de chlorure de polyvinyle et de polyéthylène chloré dans des rapports pondéraux respectifs de 10:90 à 90:10 dans lequel le chlorure de polyvinyle a une valeur de K de 45 à 80 et le polyéthylène chloré a une teneur en chlore de 30 à 45% en poids et la seconde couche étant constituée d'un adhésif, **caractérisé en ce que** la seconde couche est constituée d'un adhésif sensible à la pression, résistant aux plastifiants, comprenant le produit de réaction de polymérisation des monomères comprenant (a) 50 acide acrylique, acide méthacrylique, acrylamide et/ou méthacrylamide, (b) un acrylate d'alkyle et/ou un méthacrylate d'alkyle et (c) au moins un monomère insaturé supplémentaire.
2. Film composite selon la revendication 1, **caractérisé en ce que** le rapport pondéral du chlorure de polyvinyle : polyéthylène chloré va de 35 : 65 à 65 : 35.

3. Film composite selon les revendications 1 ou 2, caractérisé en ce que le chlorure de polyvinyle a une valeur de K allant de 50 à 65.

4. Film composite selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le polyéthylène chloré possède une teneur en chlore d'environ 42% en poids.

5. Film composite selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'adhésif est appliqué à un poids d'enrobage de 30 à 50 g/m².

6. Film composite selon l'une quelconque des revendications 1 à 5, caractérisé en ce que l'adhésif inclut de 0,5 à 5% en poids d'un phtalate dialkyle et de 10 à 35% en poids d'un ester d'acide phtalique d'alcool hydroa-
blétyle.

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